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A NEW EMPIRICAL POTENTIAL HYPERSURFACE FOR BIMOLECULAR REACTION--ETC(U)

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# A New Empirical Potential Hypersurface for Bimolecular Reaction Systems\*

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# A New Empirical Potential Hypersurface for Bimolecular Reaction Systems\*

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We have devised a fully empirical procedure for generating chemically accurate (*i.e.*, within a few kcal mol<sup>-1</sup>) potential hypersurfaces for triatomic bimolecular reaction systems. The procedure is described and applied to the H<sub>3</sub> system. Calibration of the H<sub>3</sub> empirical surface by comparison with the best *ab initio* H<sub>3</sub> surface suggests considerable utility of the empirical procedure.

## 1. INTRODUCTION

Refined and accurate *ab initio* potential energy hypersurfaces can now be obtained for simple (*i.e.*, few nuclei and few electrons) chemically reactive systems such as H<sub>3</sub>, FH<sub>2</sub>, and HLi<sub>2</sub>.<sup>1</sup> Certainly, the *ab initio* route is preferable to all other computational schemes in cases demanding modest expense (*e.g.*, less than \$10 000 in 1976 U.S. dollars) for the several hundred hypersurface points required to yield a good fit to chemically interesting regions of the surface. Nevertheless, the popularity of semi-empirical surfaces of the LEPS (London-Eyring-Polanyi-Sato) and DIM (Diatomics-In-Molecules) varieties attests to the continuing utility of inexpensive (albeit of indeterminate accuracy) surfaces in practical contexts (*e.g.*, quasiclassical trajectory studies of reaction dynamics).

We present here a fully empirical scheme for the computation of potential hypersurfaces for triatomic bimolecular reaction systems. The following sections describe our empirical approach, calibrate its accuracy by comparison to the best available H<sub>3</sub> *ab initio* ground potential hypersurface, and comment upon extensions and limitations of the method.

## 2. RÉSUMÉ OF THE MODEL

Empiricism precludes theoretical rigour. In the empirical limit, intuition replaces formal and numerical certainty. Our empirical model builds upon the set of intuitive assumptions used in the Johnston-Parr BEBO (Bond Energy-Bond Order) method<sup>2,3</sup> for the construction of collinear reaction coordinates of H-atom transfer systems:

*Assumption 1*—The amount of "chemical bonding" is constant at each point along the reaction coordinate.

*Assumption 2*—The total interaction potential is the separable sum of three two-body potentials.

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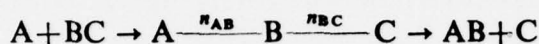
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**Assumption 3**—Empirical correlations (Pauling's rule, Badger's rule, etc.) can be used to calculate bond energies and other molecular properties from structural and spectroscopic data.

#### A. BEBO COLLINEAR REACTION COORDINATE<sup>2,3</sup>

In symbols, for the reaction:



where B is a hydrogen atom (although modified BEBO treatments have been developed for non H-atom transfers)<sup>4,5</sup> and  $n_{XY}$  is the "bond order" of diatom XY, we have:

$$n_{AB} + n_{BC} = 1, \quad (1)$$

independent of position along the reaction coordinate ( $n_{XY} = 1$  for each diatom well separated from its corresponding atom)

$$V_{\text{TOTAL}}(R_{AB}, R_{BC}) = V_{AB}(R_{AB}) + V_{BC}(R_{BC}) + V_{AC}(R_{AC}), \quad (2)$$

with the energy referenced to the  $A + BC$  limit and with  $R_{AC} = R_{AB} + R_{BC}$  for the collinear system

$$R_{XY}(n_{XY}) = R_{e,XY} - 0.26 \ln n_{XY} \text{ and} \quad (3a)$$

$$D_{XY}(n_{XY}) = D_{e,XY} n_{XY}^p \quad (\equiv V_{XY}) \quad (3b)$$

where  $R_e$  and  $D_e$  are the isolated diatom equilibrium internuclear separation and dissociation energy,  $R(n)$  and  $D(n)$  are the dressed diatom structure and dissociation energy for bond order  $n$ , and  $p$  is a "bond index" (close to unity) giving the functional dependence of bond energy upon bond order.

Using valence bond concepts, Johnston and Parr<sup>2</sup> evaluated (2) by taking  $V_{AB}$  and  $V_{BC}$  to be attractive potentials [calculated from eqn (3b)] and  $V_{AC}$  to be a repulsive potential [represented by a scaled anti-Morse fit to the Hirschfelder-Linnett calculation<sup>6</sup> of the  $H_2^*(b^3\Sigma_u^+)$  interaction energy]. They<sup>2</sup> chose to calculate the bond index from

$$p = \frac{0.26 \ln (D_e/\epsilon)}{R_m - R_e} \quad (4)$$

where  $\epsilon$  and  $R_m$  are the potential parameters (well-depth and position of the minimum) for corresponding rare gas diatoms (e.g.,  $He_2$  is the rare gas pair which is used to mimic a low bond order version of dressed  $H_2$ ). Thus, the BEBO potential energy along the collinear reaction coordinate is:

$$V(n) = D_{e,2}(1 - n^{p_2}) - D_{e,1}(1 - n)^{p_1} + D_{e,3}B(n - n^2)^{0.26\beta}[1 + B(n - n^2)^{0.26\beta}] \quad (2')$$

where  $n = n_{BC}$ ,

$$B = 0.5 \exp [-\beta \Delta R_e],$$

$\beta$  is the Morse potential parameter  $[(k_e/2D_e)^{1/2}$  where  $k_e$  is the force constant] for diatom AC,

$$\Delta R_e = R_{e,1} + R_{e,2} - R_{e,3},$$

and subscripts 1, 2, 3, are used in place of subscripts AB, BC, AC.

By comparison with *ab initio* results, Truhlar<sup>7</sup> showed that the original BEBO model (using  $p = 1.041$  for  $H_2$  and  $p = 1.036$  for  $HF$ )<sup>3</sup> generated amazingly accurate reaction coordinates and saddle point heights for  $H_3$  and  $FH_2$  systems. We update his



$H_3$  conclusions slightly in fig. 1 and 2. *Ab initio* results<sup>8</sup> given in each figure are the most accurate collinear  $H_3$  computations presently known, with stated uncertainty limits of  $\pm 0.2$  kcal mol<sup>-1</sup> in surface point energies and  $\pm 5 \times 10^{-4}$  Å in the coordinate location of the saddle point. The BEBO reaction coordinate (*i.e.*, the minimum energy path), defined by eqn (1) and (3a) is even more accurate than previously recognized<sup>7</sup> by comparison with an earlier *ab initio* computation;<sup>9</sup> the maximum deviation (at the saddle point) is now  $\sim 0.01$  Å (*cf.* fig. 1). This result is not subject to

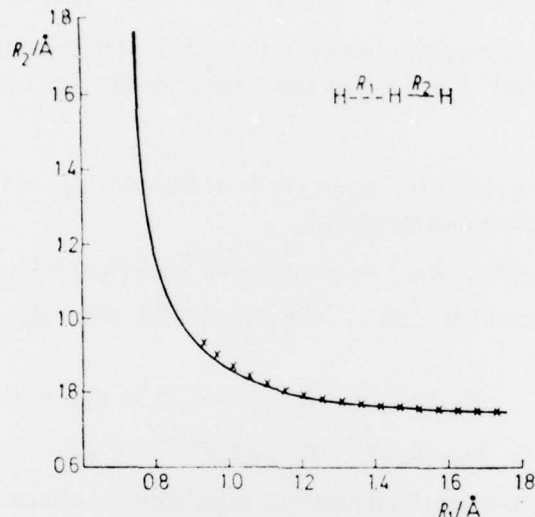


FIG. 1.—BEBO (—) reaction coordinate for ground-state  $H_3$ . *Ab initio* points (x) are from ref. (8).

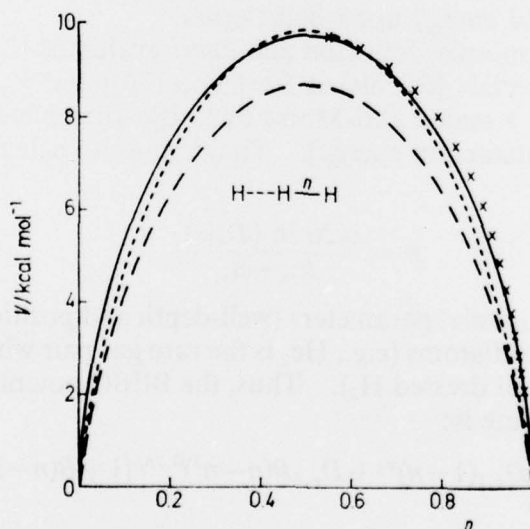


FIG. 2.—BEBO potential energy profiles for ground-state  $H_3$ . Parameters for old BEBO (—) and new BEBO I (---) and II (····) plots are described in Appendix B. *Ab initio* (x) points are from ref. (8).

updating [except perhaps through a revision of the constant appearing in Pauling's rule, eqn (3a).] The old BEBO form of the potential energy along the reaction coordinate [from eqn (2'), using  $p_{H_2} = 1.041$ ] is also strikingly accurate when compared with Bowen Liu's *ab initio* potential energy profile<sup>8</sup> (*cf.* fig. 2), but this agreement must be viewed with suspicion. Fig. 2 shows new BEBO potential energy profiles which incorporate new potential parameters for  $He_2$  derived from scattering experiments<sup>10</sup> leading to  $p_{H_2} = 0.997$  together with the *ab initio*  $H_2^*(b^3\Sigma_u^+)$  repulsive potential.<sup>11</sup>

The updated parameterization of  $p$  and  $V_{AC}$ , designated "new BEBO I" in fig. 2, gives too low a saddle point height. However, slight alteration of  $R_m$  for  $\text{He}_2$  from the best scattering potential value of  $2.963 \text{ \AA}^{10}$  to an adjusted value of  $2.93 \text{ \AA}$  increases the bond index  $p$  to a value of 1.012 and raises the collinear saddle point to close agreement with the *ab initio* result (cf. curve designated "new BEBO II" in fig. 2). These (sensitive) changes illustrate: (a) that the success of the old BEBO  $\text{H}_3$  collinear potential energy profile (based upon crude Lennard-Jones potential constants for  $\text{He}_2$  plus an inaccurate  $\text{H}_2$  repulsive potential) is partly fortuitous, and (b) that accurate potential data still yield quite reasonable saddle point heights and potential energy profiles.

We conclude that the original Johnston-Parr BEBO model<sup>2</sup> and its updated versions provide a fine representation for the  $\text{H}_3$  reaction coordinate. Numerous other systems have been treated by BEBO methods,<sup>2-5,7,12-14</sup> with the result that calculated saddle point heights are often within  $1\text{--}2 \text{ kcal mol}^{-1}$  of experimentally observed Arrhenius activation energies.<sup>15</sup>

#### B. EXTENSION OF BEBO TO FULL POTENTIAL HYPERSURFACES

We retain the BEBO picture of a triatomic reaction system  $\text{A—B—C}$  as a pair of "dressed" diatomic molecules AB and BC with repulsion between end atoms A and C. At any point along the reaction coordinate and in the vicinity of atom C, diatom AB has a bond energy that is diminished relative to the isolated molecule; the corresponding dressing of diatom BC occurs due to the presence of atom A. Eqn (3b) and (2') simply evaluate the altered diatom bond dissociation energies. For  $\text{H}_3$  (and most other reaction examples), a bond index close to unity signifies that the total attractive interaction remains nearly constant; hence, the repulsive interaction is the dominant contribution to the increase in total energy along the reaction coordinate. However, if we leave the reaction coordinate, there are other increases in total energy that we view as simply the increase in potential energy due to the displacement of dressed diatoms AB and BC from their equilibrium internuclear separations. For example, fig. 3 shows the BEBO  $\text{H}_3$  reaction coordinate and a point  $R_1, R_2$  displaced from the minimum energy path. Two reference points ( $R_{1a}, R_{2a}$  and  $R_{1b}, R_{2b}$ ) along the reaction coordinate are also indicated. With respect to point  $R_{1a}, R_{2a}$ , the dis-

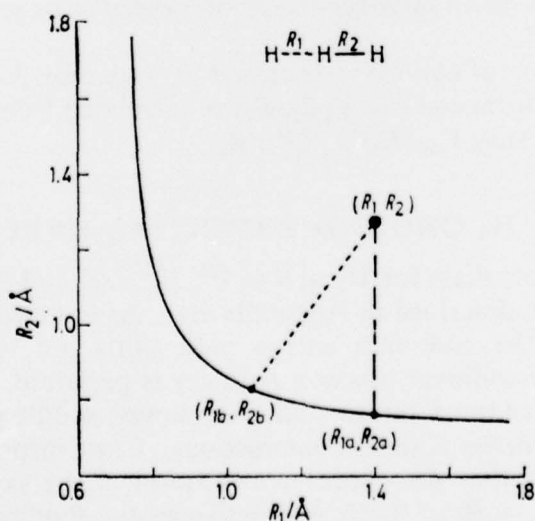


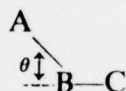
FIG. 3.—Reference point notation for extended BEBO calculations. The solid line segment is the BEBO reaction coordinate for ground-state  $\text{H}_3$ .

placed point  $R_1$ ,  $R_2$  refers to the same dressed diatom AB that was used to construct the BEBO reaction coordinate point  $R_{1a}$ ,  $R_{2a}$  (since the AB internuclear separation is unchanged) but a stretched dressed diatom BC. With respect to point  $R_{1b}$ ,  $R_{2b}$ , the displaced point  $R_1$ ,  $R_2$  refers to two stretched diatoms (AB and BC) since both AB and BC internuclear separations have altered. There is an infinity of reference points  $\{R_{1i}, R_{2i}\}$  along the reaction coordinate and the total energy depends upon the degree of stretching and/or compression associated with each choice. For all our calculations, we choose the intuitively satisfying reference point, viz., the one that minimizes the total energy:<sup>16</sup>

$$\frac{dV(R_1, R_2)}{dn_1} = 0 \quad (5)$$

where  $n_1 = 1 - n_2$  defines the bond order and hence the location of the reference point.

In the following development, we neglect the repulsive interaction  $V_{AC}$  (which is not a function of the bond order, since it depends solely on  $R_3$ ); for any geometry:



we have:

$$R_3 = [R_1^2 + R_2^2 + 2R_1R_2 \cos \theta]^{1/2} \quad (6)$$

and  $V_{AC}(R_3)$  is determined either from a scaled anti-Morse function<sup>2,3</sup> or from our fit to the *ab initio*  $H_2^+(b^3\Sigma_u^+)$  potential.<sup>11</sup> The total energy excluding repulsion is:

$$V(R_1, R_2) = -D_1^0 - D_2^0 + M_1 + M_2 \quad (7)$$

where

$$M_i = D_i^0 \{1 - \exp[-\beta_i^0(R_i - R_i^0)]\}^2 \quad (8)$$

$$\beta_i^0 = (k_{e,i}^0/2D_i^0)^{1/2} \quad (9)$$

and

$$k_{e,i}^0 = \exp(\gamma_i + \delta_i R_i^0). \quad (10)$$

Reference diatom quantities  $D_i^0$ ,  $R_i^0$ , and  $p_i$  are evaluated from eqn (3) and (4). The Herschbach-Laurie version<sup>17</sup> of Badger's rule,<sup>18</sup> eqn (10), is used to calculate dressed reference diatom force constants  $k_{e,i}^0$ ; the parameters  $\gamma_i$  and  $\delta_i$  are determined from a fit to experimental data on an inter-related set of molecules or several electronic states of the same molecule.<sup>19</sup>

The iterative solution of eqn (5) is discussed in Appendix A. Once the reference value  $n_1$  is determined from eqn (5),  $V(R_1, R_2)$  is calculated from eqn (3), (4) and (7). The total energy is the sum  $V_{AC}(R_3) + V(R_1, R_2)$ .

### 3. EXAMPLE: $H_3$ GROUND POTENTIAL HYPERSURFACE

Fig. 4 shows equipotentials for  $H_3$  at  $\theta = 0^\circ$ ,  $30^\circ$ ,  $60^\circ$  and  $90^\circ$  calculated by our empirical procedure (as described in Appendix B). As  $\theta$  increases, the saddle point height increases and the minimum energy path shifts out to larger internuclear separations; hence the collinear reaction pathway is preferred. Within the context of BEBO empiricism, collinear surfaces have the lowest saddle point energies due to the purely repulsive character of the AC interaction. Close inspection of the collinear surface in fig. 4 reveals that the coordinate location of the saddle point is slightly shifted outward (to  $R_1 = R_2 = 0.956$  Å) relative to the Pauling rule<sup>20</sup> result [from eqn (3a),  $R_1 = R_2 = 0.922$  Å]. This shifting is due to the relative steepness of attractive ( $V_{AB}$ ,  $V_{BC}$ ) and repulsive ( $V_{AC}$ ) interactions. For  $H_3$ , the anti-Morse



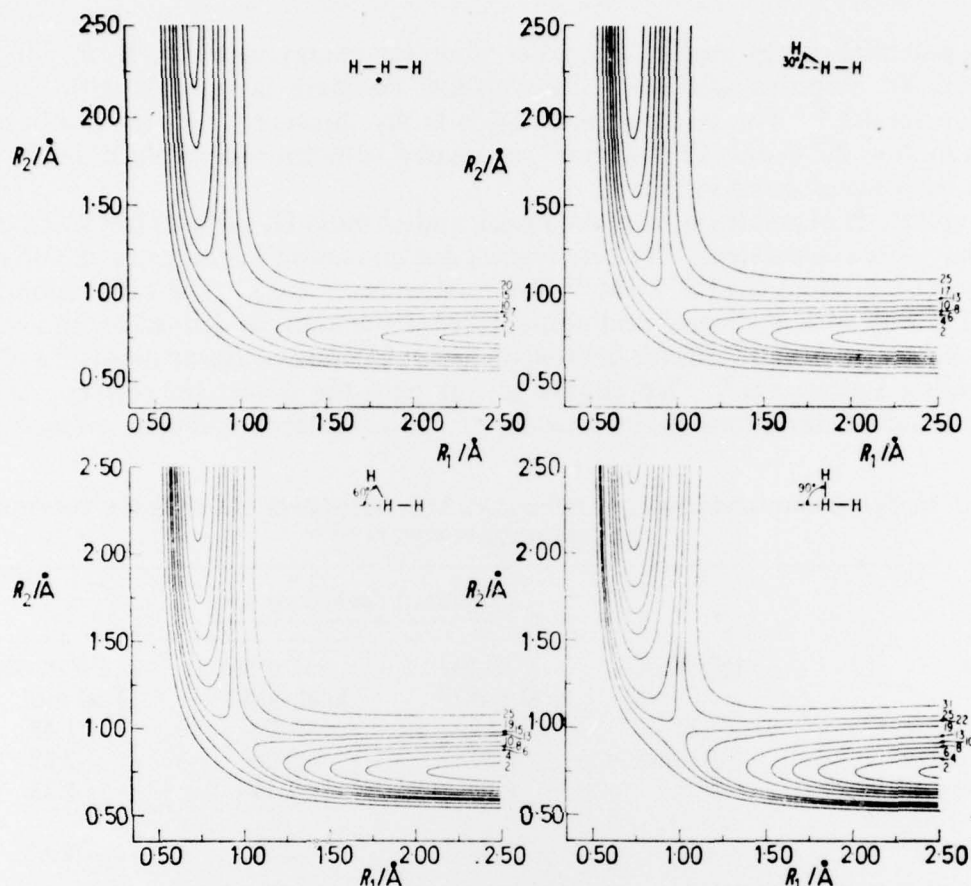


FIG. 4.—Empirical potential hypersurfaces ( $\theta = 0^\circ, 30^\circ, 60^\circ$  and  $90^\circ$ ) for ground-state  $H_3$ .

repulsion listed in Appendix B rises steeply as  $R_3$  decreases, while the Morse attractions are quite modest since  $\partial M_i / \partial R_i \sim 0$  in the vicinity of  $R_i^0$ .

It is important to obtain an assessment of the quantitative success of the empirical

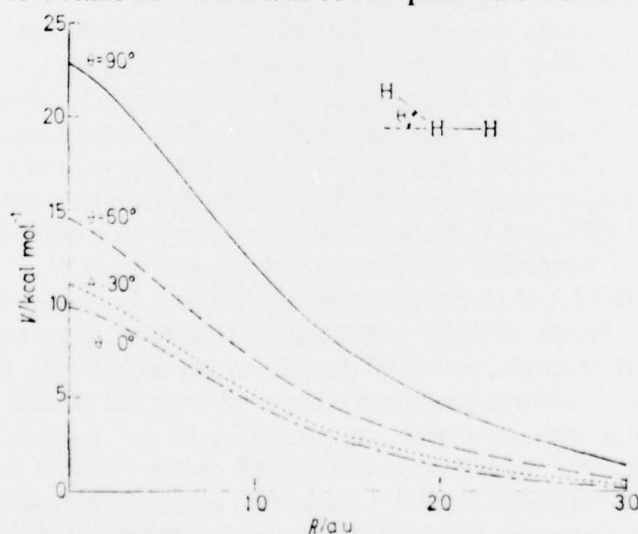


FIG. 5.—Potential energy profiles along the minimum energy paths of empirical  $H_3$  ground hypersurfaces.

surface we have constructed; this assessment can best be accomplished by comparison of both its static and dynamic characteristics relative to those of the best  $H_3$  *ab initio* surface.<sup>8</sup> One static calibration involves the shape of minimum energy paths. Fig. 5

shows potential energy profiles along the minimum energy paths for  $H_3$   $\theta = 0^\circ, 30^\circ, 60^\circ$  and  $90^\circ$  empirical surfaces; these profiles compare favourably with accurate *ab initio* results.<sup>21</sup> The bending potential is faulty, however (e.g., the saddle point height for  $\theta = 90^\circ$  is only 23 kcal mol<sup>-1</sup> compared with approximately 30 kcal mol<sup>-1</sup> for an accurate *ab initio* surface<sup>22</sup>).

A multitude of empirical, semi-empirical, and *ab initio*  $H_3$  surfaces [reviewed in ref. (23)] have been calculated. We here restrict our discussion to comparison with a few widely-used surfaces (LEPS, DIM,<sup>24</sup> Porter-Karplus,<sup>25</sup> etc.). The calibration is always Liu's *ab initio* collinear<sup>8</sup> and non-collinear<sup>22</sup> surfaces, as defined by an array of 137 collinear points and surface fit<sup>8</sup> together with 115 non-collinear points<sup>22</sup> and corresponding surface fits.<sup>26</sup> We choose to compare the points themselves; table 1 shows standard deviations of the energies of various surface points as a function of

TABLE 1—STANDARD DEVIATIONS OF EMPIRICAL AND SEMI-EMPIRICAL SURFACE POINTS FROM LIU CALIBRATION POINTS.<sup>8,22</sup>

surface	reference	standard deviations for:		
		$V \leq 20/$ kcal mol <sup>-1</sup>	$V \leq 30/$ kcal mol <sup>-1</sup>	$V \leq 40/$ kcal mol <sup>-1</sup>
Yates-Lester <sup>a</sup>	21	1.15	1.28	1.48
Kafri-Berry	this work	1.52	2.20	2.82
improved LEPS	<sup>b</sup>	1.12	1.17	1.38
Porter-Karplus, surface 2 <sup>c</sup>	25	1.83	2.38	2.63

<sup>a</sup> This surface is intended to be an accurate fit to Liu calibration points. <sup>b</sup> London-Eyring-Polanyi-Sato form incorporating *ab initio* repulsion<sup>11</sup> plus modified Morse attraction (see Appendix B); Sato parameter adjusted to 0.025 8 to yield the correct saddle point height. <sup>c</sup> The most popular version of this potential.<sup>23</sup>

maximum potential energy sampled. For  $V \leq 20, 30$  and  $40$  kcal mol<sup>-1</sup>, samples of 145, 175 and 214 *ab initio* points<sup>8,22</sup> are available. Probably, only points below a maximum potential energy of 20 kcal mol<sup>-1</sup> are important for thermal reaction processes. We are carrying out quasiclassical trajectory computations to gauge the dynamical accuracy of various  $H_3$  surfaces;<sup>27</sup> at this time, we note that our empirical surface is simple and inexpensive to use in such dynamical computations.

In contrast to LEPS and Porter-Karplus surfaces which contain adjustable parameters, the present empirical surface (based on old BEBO<sup>2,3</sup>) is not adjustable. However, new BEBO I and II reaction coordinates (see fig. 2 and Appendix B) which incorporate much better defined potential parameters apparently do not yield better surfaces; for example, standard deviations are about 50% higher for  $V \leq 20, 30$  and  $40$  kcal mol<sup>-1</sup> calibration points compared with old BEBO results.

Another popular surface which, in principle, is not adjustable is DIM (Diatomics-In-Molecules).<sup>24</sup> Recent extended DIM results<sup>28</sup> show that the method is stable to basis set variation and is reasonably accurate provided that an *ad hoc* neglect of overlap factors is adopted. The best agreement of extended DIM was found for cases I(a) and II(a) [see ref. (28)] which predicted collinear saddle point heights of 12.5 and 12.0 kcal mol<sup>-1</sup>. We can anticipate that standard deviations of DIM points from Liu *ab initio* points<sup>8,22</sup> will be somewhat higher than the surfaces considered in table 1.

Standard deviations may be misleading, since they are sensitive to both

coordinate and energy errors (*e.g.*, a trial surface isomorphous to the true surface, but shifted significantly in coordinate space, would display large standard deviations; reaction dynamics computations using such an isomorphous surface would, however, probably be quite accurate). In lieu of dynamical computations, a better measure of surface suitability for treatment of reactive processes might be the accuracy of the isotropic (*i.e.*, spherically symmetric) part of the potential, now known experimentally for  $H_3$ .<sup>29</sup> Fig. 6 shows the experimental  $V_0$  together with Porter-Karplus, Yates-Lester and our  $V_0$  values;<sup>30</sup> we seem to be in quite close accord with experiment.

#### 4. SOME PROJECTIONS AND CONCLUSIONS

We have empirically treated various other systems ( $FH_2$ ,  $CNH_2$ , etc.) with as much apparent success as for  $H_3$ . The old BEBO<sup>2,3</sup> prescription for the collinear reaction coordinate seems to guarantee reasonable saddle point heights and geometries,<sup>2-5,7,12-14</sup> even though the treatment of the triplet repulsion between end atoms is dubious. We have also been able to extend our empirical surface to 4-atom systems such as  $H_2 + D_2$ , but calibration of the results is difficult for these more complex cases.

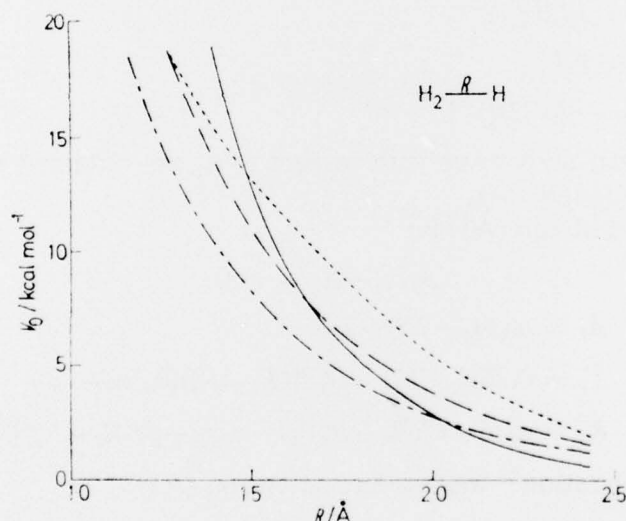


FIG. 6.—Spherically symmetric (*i.e.*, isotropic) part of the  $H_2-H$  potential. Sources of data are identified in table 1; experimental data are from ref. (29). — experimental, — — Kafri-Berry, - - - Yates-Lester, — · — Porter-Karplus.

Extensions of the empirical approach described in this paper to non-reactive and excited potential hypersurfaces appear feasible. At present, we cannot recommend a good procedure for dealing with multi-valent atoms (*e.g.*, oxygen atom in water) and/or systems with preferred non-collinear paths.

The greatest utility of our empiricism may well be for the treatment of reactive collisions of simple triatomic systems, but this application remains to be tested and documented.

We wish to thank Drs. Bowen Liu, George Schatz, Don Heller and B. H. Choi and Profs. Phil Certain, K. T. Tang and Don Truhlar for discussions and materials.

## APPENDIX A:

## SOLUTION OF EQUATION (5)

In order to solve eqn (5) to find  $n_1$  and, hence, the reference point along the reaction coordinate (via eqn (3a)), we take partial derivatives:

$$\frac{dV(R_1, R_2)}{dn_1} = \sum_{i=1}^2 \left[ \frac{-\partial D_i^0}{\partial n_1} + \frac{\partial M_i}{\partial R_i^0} \frac{\partial R_i^0}{\partial n_1} + \frac{\partial M_i}{\partial D_i^0} \frac{\partial D_i^0}{\partial n_1} + \frac{\partial M_i}{\partial \beta_i^0} \left( \frac{\partial \beta_i}{\partial k_{e,i}^0} \frac{\partial k_{e,i}^0}{\partial R_i^0} \frac{\partial R_i^0}{\partial n_1} + \frac{\partial \beta_i^0}{\partial D_i^0} \frac{\partial D_i^0}{\partial n_1} \right) \right] = 0. \quad (A1)$$

From eqn (3), (7), (8), (9) and (10), we have:

$$\partial D_i^0 / \partial n_1 = p_i D_i^0 / n_1 \quad (A2)$$

$$\partial M_i / \partial n_1 = -2\beta_i^0 D_i^0 \exp[-\beta_i^0(R_i - R_i^0)] \{1 - \exp[-\beta_i^0(R_i - R_i^0)]\} \quad (A3)$$

$$\partial R_i^0 / \partial n_1 = -0.26 / n_1 \quad (A4)$$

$$\partial M_i / \partial D_i^0 = M_i / D_i^0 \quad (A5)$$

$$\partial M_i / \partial \beta_i^0 = 2(R_i - R_i^0) D_i^0 \exp[-\beta_i^0(R_i - R_i^0)] \{1 - \exp[-\beta_i^0(R_i - R_i^0)]\} \quad (A6)$$

$$\partial \beta_i^0 / \partial k_{e,i}^0 = \beta_i^0 (2k_{e,i}^0)^{-1} \quad (A7)$$

$$\partial k_{e,i}^0 / \partial R_i^0 = \delta_i k_{e,i}^0 \quad (A8)$$

$$\partial \beta_i^0 / \partial D_i^0 = -\beta_i^0 (2D_i^0)^{-1}. \quad (A9)$$

Corresponding partial derivatives with respect to  $n_2$  are obtained via eqn (1) which yields the ratio:  $\partial n_2 / \partial n_1 = -1$ .

The explicit form of eqn (A1) is:

$$A_1/n_1 - A_2/n_2 = 0 \quad (A10)$$

where  $A_i = p_i(M_i - D_i^0) + T_i K_i \quad (A11)$

$$T_i = 0.26(2D_i^0\beta_i^0) + D_i^0\beta_i^0(R_i - R_i^0)(0.26\delta_i - p_i) \quad (A12)$$

and  $K_i = \exp[-\beta_i^0(R_i - R_i^0)] \{1 - \exp[-\beta_i^0(R_i - R_i^0)]\}. \quad (A13)$

Newton-Raphson iteration<sup>31</sup> was used to solve eqn (A1):

$$n_{j+1} = n_j - F(\partial F / \partial n_1)^{-1} \quad (A14)$$

where

$$F = \partial V(R_1, R_2) / \partial n_1 \quad (A15)$$

$$\partial F / \partial n_1 = (Q_1 - A_1)/n_1^2 + (Q_2 - A_2)/n_2^2 \quad (A16)$$

and  $Q_i = p_i A_i + T_i K_i (0.26\delta_i - p_i) / 2 + p_i T_i K_i + 0.26\beta_i^0 K_i (0.26\delta_i - p_i) D_i^0 - 2D_i^0 \{\beta_i^0 [0.26 + (R_i - R_i^0)(0.26\delta_i - p_i) / 2]\}^2 \exp[-\beta_i^0(R_i - R_i^0)] \{1 - 2\exp[-\beta_i^0(R_i - R_i^0)]\}. \quad (A17)$

To start the iteration, we use the initial condition:

$$n_{1, \text{start}} = n_1^0 / (n_1^0 + n_2^0) \quad (A18)$$

with  $n_i^0 = \exp[(R_{e,i} - R_i) / 0.26]. \quad (A19)$

Convergence ( $n_{j+1} - n_j \leq 10^{-5}$ ) is typically reached after 3 iterations.



## APPENDIX B:

H<sub>3</sub> SURFACE PARAMETERS

Three sets of H<sub>3</sub> surfaces were calculated by using old BEBO, new BEBO I, and new BEBO II collinear reaction coordinates (*cf.* fig. 2). In all sets, we took:  $D_i^0 = 109.5 \text{ kcal mol}^{-1}$ ,  $R_{e,i} = 0.7412 \text{ \AA}$ , and  $k_{e,i}^0 = 286 \exp(4.00 - 0.25R_i^0) \text{ kcal mol}^{-1} \text{ \AA}^{-2}$ . For old BEBO,  $p_i = 1.041$  and  $V_{AC} = 0.25D_i^0\{\exp[-2\beta_i^0(R_3 - R_i^0)] + 2\exp[-\beta_i^0(R_3 - R_i^0)]\}$ . For new BEBO I,  $p_i = 0.996$  and  $V_{AC}$  is the *ab initio* repulsion.<sup>11</sup> For new BEBO II,  $p_i = 1.012$  with the same *ab initio* repulsion. Fig. 4 shows old BEBO computations.

For most surface calculations, we employed Morse functions for  $M_1$  and  $M_2$  in eqn (7). However, the Morse function for  $H_2(X^1\Sigma_g^+)$  is a poor fit to the *ab initio* potential<sup>32</sup> at  $R < R_e$  and even deviates significantly (by more than  $4 \text{ kcal mol}^{-1}$ ) at long range ( $\sim 2 \text{ \AA}$ ). For the thermal  $H + H_2$  reaction (*i.e.*, for surface points below  $20 \text{ kcal mol}^{-1}$ ), the inadequacies of the  $H_2$  Morse function are not serious, but higher energy processes require a better potential fit.

We have devised a modified Morse function for  $H_2(X^1\Sigma_g^+)$  which is accurate to better than  $0.5 \text{ kcal mol}^{-1}$  at  $R > 0.57 \text{ \AA}$ :

$$M_i = D_i^0\{1 - \exp[-\beta_i^0(R_i - R_i^0)(1 + L_i)]\}^2 \quad (\text{B1})$$

$$\text{where} \quad L_i = b_0 \exp[-b_1(R_i - R_i^0 - b_2)^2] \quad (\text{B2}).$$

$$\begin{aligned} \text{At } R < R_i^0: \quad & b_0 = 0.019\,959\,95 \\ & b_1 = -2.217\,032\,9 \\ & b_2 = 0.512\,704\,12 \end{aligned}$$

$$\begin{aligned} \text{while at } R \geq R_i^0: \quad & b_0 = 0.283\,162\,54 \\ & b_1 = 0.836\,707\,93 \\ & b_2 = 2.251\,996\,4. \end{aligned}$$

All three H<sub>3</sub> surfaces (old BEBO, new BEBO I, and new BEBO II) use the modified Morse potential. Solution of eqn (A1) requires a slight alteration of working equations given in Appendix A since  $M_i$  has a different form. We shall present details of the modified Morse fitting procedure and hypersurface calculations elsewhere.

<sup>1</sup> For collected references, see:

J. N. L. Connor, *Ann. Rep. Prog. Chem.*, 1974, **70**, 5 and G. G. Balint-Kurti, *Adv. Chem. Phys.*, 1975, **30**, 137.

<sup>2</sup> H. S. Johnston and C. Parr, *J. Amer. Chem. Soc.*, 1963, **85**, 2544.

<sup>3</sup> H. S. Johnston, *Gas Phase Reaction Rate Theory* (Ronald Press, New York, 1966).

<sup>4</sup> S. W. Mayer, L. Schieler and H. S. Johnston, in *Eleventh Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, 1967), p. 837.

<sup>5</sup> S. W. Mayer, *J. Phys. Chem.*, 1969, **73**, 3941.

<sup>6</sup> J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.*, 1950, **18**, 130.

<sup>7</sup> D. G. Truhlar, *J. Amer. Chem. Soc.*, 1972, **94**, 7584.

<sup>8</sup> B. Liu, *J. Chem. Phys.*, 1973, **58**, 1925.

<sup>9</sup> I. Shavitt, R. M. Stevens, F. L. Minn and M. Karplus, *J. Chem. Phys.*, 1968, **48**, 2700.

<sup>10</sup> J. M. Farrar and Y. T. Lee, *J. Chem. Phys.*, 1972, **56**, 5801.

<sup>11</sup> W. Kolos and L. Wolniewicz, *J. Chem. Phys.*, 1965, **43**, 2429. The  $H_2(b^3\Sigma_u^+)$  potential was fit over the range 1–7 bohr by:



$$V_{AC} = \exp(a_0 + a_1 R + a_2 R^2 + a_3 R^3 + a_4 R^4 + a_5 R^5)$$

with  $a_0 = 13.374\,412\,72$

$a_1 = -2.897\,084\,794$

$a_2 = 1.170\,623\,019$

$a_3 = -0.379\,778\,752$

$a_4 = 0.056\,206\,142$

$a_5 = -0.003\,245\,39$

[energies are in  $\text{cm}^{-1}$  and internuclear separations in a.u. (1 a.u. =  $0.529\,177\,06\,\text{\AA}$ )].

- <sup>12</sup> S. W. Mayer, L. Schieler and H. S. Johnston, *J. Chem. Phys.*, 1966, **45**, 385.
- <sup>13</sup> S. W. Mayer and L. Schieler, *J. Phys. Chem.*, 1968, **72**, 236, 2628.
- <sup>14</sup> N. L. Arthur and J. A. McDonell, *J. Chem. Phys.*, 1972, **56**, 3100; 1972, **57**, 3228; N. L. Arthur, K. F. Donchi, and J. A. McDonell, *J. Chem. Phys.*, 1975, **62**, 1585.
- <sup>15</sup> Saddle point heights of potential energy hypersurfaces are not equivalent to activation energies of bimolecular reactions [cf., M. Menzinger and R. Wolfgang, *Angew. Chem. (Int. Edn.)*, 1969, **8**, 438], but the differences between these quantities are small enough to ignore for the present discussion.
- <sup>16</sup> Eqn (5) defines an extremum, but for reasonable starting values of the bond order, this extremum is always a unique minimum; hence, it is not necessary to solve second derivative equations.
- <sup>17</sup> D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, 1961, **35**, 458.
- <sup>18</sup> R. M. Badger, *J. Chem. Phys.*, 1934, **2**, 128; 1935, **3**, 710.
- <sup>19</sup> See Section 4.F of ref. (3) for details.
- <sup>20</sup> L. Pauling, *J. Amer. Chem. Soc.*, 1947, **69**, 542.
- <sup>21</sup> A. C. Yates and W. A. Lester, Jr., *Chem. Phys. Letters*, 1974, **24**, 305.
- <sup>22</sup> B. Liu, personal communication.
- <sup>23</sup> D. G. Truhlar and R. E. Wyatt, *Adv. Chem. Phys.*, 1977, **36**.
- <sup>24</sup> F. O. Ellison, N. T. Huff and J. C. Patel, *J. Amer. Chem. Soc.*, 1963, **85**, 3544.
- <sup>25</sup> R. N. Porter and M. Karplus, *J. Chem. Phys.*, 1964, **40**, 1105.
- <sup>26</sup> G. C. Schatz, personal communication.
- <sup>27</sup> O. Kafri and M. J. Berry, in progress.
- <sup>28</sup> E. Steiner, P. R. Certain and P. J. Kuntz, *J. Chem. Phys.*, 1973, **59**, 47.
- <sup>29</sup> R. Gengenbach, Ch. Hahn, and J. P. Toennies, *J. Chem. Phys.*, 1975, **62**, 3620.
- <sup>30</sup>  $V_e$ 's are replotted from fig. 7 of: B. H. Choi and K. T. Tang, *J. Chem. Phys.*, 1975, **63**, 2854.
- <sup>31</sup> See, for example, A. Ralston, *A First Course in Numerical Analysis*, (McGraw-Hill, New York, 1965).
- <sup>32</sup> See W. Kolos and L. Wolniewicz, *J. Mol. Spectr.*, 1975, **54**, 303 and references cited therein.

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